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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

MUNEKATA ET AL

Application No.: 10/666,129

Art Urdt: 1742

Filed:

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Examiner: Sikyin Ip

For:

LEAD-FREE SOLDER ALLOY

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

Dear Sir:

- L Yoshitaka Toyoda, declare as follows:
- I am one of the joint inventors of the above-identified patent application.
- I graduated from Chiba Institute of Technology in 1989 with a bachelor of science degree. My area of specialization was metallurgy.
- 3. I have been an employee of Senju Metal Industry Co., Ltd., which is the assignee of the present application, since 1989. I currently work in the Research Center of Senju. My primary duties are the research and development of lead-free solder alloys for use in the manufacture of electronic devices.
- 4. I am a co-inventor of 17 Japanese patent applications and patents and six United States patent applications and patents. I am also a co-author of 5 scientific papers related to

solder alloys which have been presented at international symposiums in China, Japan, and the United States.

- 5. In the past, solder alloys for use in electronic devices were primarily lead-containing solders. Lead-containing solders were considered advantageous on account of their low melting point and good wettability. However, lead-containing solders pose environmental problems, and the use of lead-containing solders is being increasingly regulated. As a result, there is a strong movement in the electronics industry towards the use of lead-free solders.
- 6. Lead-free solders typically have a significantly higher melting temperature than lead-containing solders. For example, a 63SnPb entectic solder, which is a common lead-based solder, has a liquidus temperature of 183°C, while a Sn3.0Ag0.5Cu solder, which is commonly used in the electronics industry as a lead-free solder, has a liquidus temperature of about 220°C. The maximum temperature to which many electronic devices can be exposed during manufacture is typically around 240°C. The temperature at which flow soldering takes place is always at least 30°C higher than the liquidus temperature of the solder being used. This means that the margin between the soldering temperature and the maximum temperature to which electronic parts can be exposed is much smaller for lead-free solders than for lead-containing solders. Due to the smaller temperature margin for lead-free solders, when soldering an electronic part with a lead-free solder, it is desirable for the soldering to be carried out as quickly as possible to minimize the length of time to which the electronic part is exposed to a high temperature and thereby reduce the chances of the electronic part undergoing thermal damage.
- 7. When performing flow soldering and reflow soldering, one method of lowering the length of time required for soldering is to increase the wettability of the solder.
- 8. It is known in the soldering industry that the addition of Ag to a Sn-Cu based solder improves wettability. For this reason, SnAgCu-based solders have been the predominant form of lead-free solders used in flow soldering and reflow soldering in Japan. According to statistics of the Japan Electronic Information Technology Association, as of January 1, 2003, SnAgCu-based solders were the most common solders used for reflow

soldering and flow soldering.

- 9. Although Ag has a good effect on wettability, since Ag is a precious metal, it has the drawback that it is expensive. Also, the addition of Ag can impair the surface properties of solder and result in the formation of wrinkles.
- 10. Thus, the situation existing in the electronics industry prior to the present invention was that there was a strong but unsatisfied need for a solder alloy having wettability comparable to that of a SnAgCu-based solder but which does not require Ag.
- 11. My fellow inventors and I discovered that the addition of very small amounts of P to a SnCu-based lead-free solder alloy produces large improvements in wettability. The improvements are comparable or close to those produced by the addition of Ag, but the improvements are achieved at a much lower cost than when Ag is used.
- 12. In the electronics industry, a widely-accepted indicator of the wettability of solder for flow soldering is the zero crossing time measured by the meniscograph method. The test procedures for this method are described in JIS 3197. In this test, a metal test piece is dipped into a solder bath. The force exerted on the test piece by the molten solder in the solder bath is measured. In this test, the measured force starts at zero and decreases (becomes negative) until it reaches a minimum. Then, as the solder wets the test piece, the measured force increases from the minimum value. As it increases, it momentarily becomes zero again, and then the force continues to increase and becomes a positive value. The length of time from the start of the test until the measured force momentarily becomes zero again is called the "zero crossing time". The lower the zero crossing time, the better is the wettability of the solder.
- 13. Exhibit 1 is a graph showing the results of a wettability test by the meniscograph method which I conducted at the laboratories of Senju. The test procedures were similar to those set forth in JIS 3197. Exhibit 1 shows the results for 8 different SnCu-based alloys. Each alloy contained Ge, Ag, or P as an additive to increase wettability. The compositions of various solder alloys which were tested are shown along the horizontal axis, and a scale of time in seconds is marked along the vertical axis. Each circle in the graph indicates the

average of the measurements of zero crossing time for five samples having the same solder composition, and the horizontal lines above and below the circle indicate the standard deviation for those samples.

- 14. The following observations can be made from the data shown in Exhibit 1:
- (a) The addition of Ge has much less effect on wettability than does the addition of Ag or P. This shows that even though Ge and P are both added to solders to inhibit oxidation, they have different effects on wettability.
 - (b) The zero crossing time is markedly decreased by the addition of Ag.
- (c) The addition of P shortens the zero crossing time more than does the addition of a small amount of Ag. The addition of a large amount of Ag can shorten the zero crossing time more than can the addition of a small amount of P.
- (d) Even when an extremely small amount of P, i.e., 0.001 0.1% of P, is added, the zero crossing time is shortened more than by the addition of 0.1% Ag, and in this range for P, the same zero crossing time is obtained as with the addition of 0.3% Ag.
- 15. From Exhibit 1, it can be seen that P is extremely effective at improving the wettability of a SnCu-based solder.
- 16. Exhibit 2 is a graph of the results of another wettability test by the meniscograph method which I performed on various solder alloys. It shows the effects of different concentrations of P on wettability. This test was performed by the same procedure as the test described with respect to Exhibit 1.
- 17. Exhibit 3 is a graph showing the zero crossing time for the three SnCuNiP alloys of Exhibit 2 and for a fourth SnCuNiP alloy containing 0.5% P. A least squares curve is drawn through the data points.
- 18. Exhibit 3 shows that with a Sn0.7Cu0.1NiP alloy, the zero crossing time is lowest when the P content is between 0.01 and 0.02 weight %.
- 19. As of March 2004, the unit cost of Ag was approximately 26,000 yen per kg, while the unit cost of P in the form of a Sn-P mother alloy was approximately only 160 yen

per kg, or only about 0.6 % of the unit cost of Ag. This means that a SnCuNiP providing wettability comparable to a SnCuNiAg alloy can be manufactured at a much lower material cost.

20. As shown by Exhibits 2 and 3, in the wettability tests which I performed, the zero crossing time for a Sn0.7Cu0.1Ni alloy was approximately 5.2 seconds, and the zero crossing time for a Sn0.7Cu0.1Ni0.5P alloy was approximately 4.7 seconds. From these values for zero crossing time corresponding to a P content of 0% or 0.5% (which are outside the range of P in the pending claims of the present application), I do not believe that a person skilled in the art could predict the marked effects on wettability of a P content in the range of 0.001 to 0.1 wt%.

21. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully submitted,

Yoshitaka Toyoda Yoshitaka Toyoda Satte City, Japan

Date: March 17 2005

Attached exhibits: Exhibits 1 - 3